

## Complex Formation of Crown Ethers with Cations in the Water–Organic Solvent Mixtures. Part VII. Thermodynamic of Interactions of Na<sup>+</sup> Ion with 15-Crown-5 Ether in the Mixture of Water with *N,N*-Dimethylacetamide at 298.15 K

MAŁGORZATA JÓŹWIAK

*Department of Physical Chemistry, University of Lodz, Pomorska 165, 90-236 Lodz, Poland. E-mail: mjozwiak@uni-lodz.pl*

(Received 7 July 2003; in final form 20 March 2004)

**Key words:** complex of 15-crown-5 with sodium cation, enthalpy of solution, entropy–enthalpy relationship, *N,N*-dimethylacetamide–water mixture, solvation of complex, thermodynamic functions of complex formation

### Abstract

The thermodynamic functions of the complex formation of 15-crown-5 ether with sodium cation in mixtures of water with *N,N*-dimethylacetamide at 298.15 K are calculated. The equilibrium constants of complex formation of 15-crown-5 ether with sodium cation have been determined by conductivity measurements. The enthalpic effect of complex formation has been measured by a calorimetric method at 298.15 K. The complexes are enthalpy-stabilized but entropy-destabilized in this mixed solvent. A quantitative dependence of the excess molar enthalpy and entropy of complex formation on the structural and energetic properties of interactions between water and organic solvent molecules in the mixtures of water with *N,N*-dimethylacetamide, *N,N*-dimethylformamide and dimethylsulfoxide has been found. The linear entropy–enthalpy relationship for complex formation is also presented. The solvation enthalpy of the complex in the water–*N,N*-dimethylacetamide mixtures is discussed.

**Abbreviations:** AN – acetonitrile; B15C5 – benzo-15-crown-5 ether; B15C5/Na<sup>+</sup> – complex of benzo-15-crown-5 ether with sodium cation; *c* – concentration in mol dm<sup>-3</sup> of solution;  $C_{p2}^0$  – partial molar heat capacity of a substance in water; DMA – *N,N*-dimethylacetamide; DMF – *N,N*-dimethylformamide; DMSO – dimethylsulfoxide;  $H^E$  – excess molar heat of mixing water with organic solvent;  $h_{22}$  – the enthalpic homogeneous pair interaction coefficient;  $K_f$  – equilibrium constant of complex formation; M – mixed water–organic solvent;  $T\Delta_f S_0$  – intrinsic entropy gain upon complexation for each ligand mainly attributed to the desolvation of the complexed cation; W – water;  $V_{\phi_{22}}$  – slope of apparent molar volume *versus* the molarity of organic substance;  $V^E$  – excess molar volume of the mixture;  $x_w$  – mole fraction of water;  $\alpha$  – quantitative measure of the extent of the entropic cancelling effect attributed to strong or weak bonding as a result of enthalpy changes due to the cation–ligand interactions;  $\Delta_{\text{sol}}H_2$  – dissolution enthalpies of 15C5 in the water–organic solvent mixture with NaI;  $\Delta_f G^0$  – free energy of complex formation;  $\Delta_f H^0$  – standard enthalpy of complex formation;  $\Delta_f H_{(s)}$  – enthalpy of complex formation in the solution;  $\Delta_{\text{tr}}H$  – enthalpy of transfer;  $\Delta_f S^0$  – standard entropy of complex formation;  $\Lambda_{\text{obs}}$  – observed molar conductance of NaI solution during conductometric titration;  $\delta\Delta_f H_{(s)}$  – difference between the enthalpy of complex formation in the water–organic mixed; solvent and that in water; 15C5 – 15-crown-5 ether; 15C5/Na<sup>+</sup> – complex of 15-crown-5 ether with sodium cation.

### Introduction

The present study is a continuation of investigations undertaken in our laboratory to examine how the properties of mixed solvent influence the formation of complexes of ligands with cations [1–4]. The performed studies consisted of observing the changes in thermodynamic functions of the complex formation during the addition of water to an organic solvent. The water–organic solvent mixtures used in these studies are of particular interest due to different capabilities to solvate

cations and crown ethers by the mixture components [5–8]. The studies previously performed concerned thermodynamic functions of the formation of 15-crown-5 ether (15C5) and benzo-15-crown-5 ether (B15C5) complexes with sodium cation (Na<sup>+</sup>) (15C5/Na<sup>+</sup> and B15C5/Na<sup>+</sup>) in the mixtures of water with acetonitrile (AN) [3, 9], dimethylsulfoxide (DMSO) [1,2] and *N,N*-dimethylformamide [4]. Quantitative relationships were found between some of these functions and the acid–base properties of the mixtures used for the studies.

The present paper relates the examination of the thermodynamic functions of 15C5/Na<sup>+</sup> complex formation in the mixture of water with *N,N*-dimethylacetamide (DMA) as a solvent with hydrophobic properties [10]. It was attempted to find a quantitative relationship between the thermodynamic functions of complex formation and the functions representing the structural and energetic properties of interactions between water and organic solvent molecules in the mixtures of water with DMA, DMF and DMSO.

## Experimental

15-crown-5 ether (15C5) (Aldrich) 98% was used as received. *N,N*-dimethylacetamide (Aldrich 99%) was purified and dried by the method described in the literature [11]. Sodium iodide (NaI) (Fluka) for analysis >99.5% was dried at 323 K under vacuum. The water content in the water–organic solvent mixtures was from 0 to 100 mol%.

To obtain the thermodynamic functions of complex formation two methods have been used: the conductometric titration to find the equilibrium constant of complex formation and calorimetric measurements to calculate the enthalpy effect of complex formation.

### Conductometric measurements

Conductometric measurements were carried out using a Wayne Kerr Automatic Precision Bridge B905 (England) with a frequency of 10 kHz. Details of the system and measuring procedure are given in previous papers [1, 12]. The conductivity of the NaI solution was measured at 298.15 K with the error of measured conductance value  $\pm 0.001 \text{ S cm}^2$  and it was  $\pm 0.005 \text{ S cm}^2 \text{ mol}^{-1}$  for the molar conductivity. The initial concentration of NaI was  $(0.00079 \pm 0.00007) \text{ mol dm}^{-3}$  and the concentration of 15C5 was from  $0.00009 \text{ mol dm}^{-3}$  to  $0.00528 \text{ mol dm}^{-3}$ . Twenty-eight to thirty portions of 15C5 solution were added to the NaI solution for one titration. The results of molar conductivity as a function of molar ratio  $c_{15C5}/c_{NaI}$  are presented in Table 1.

### Dissolution enthalpies of 15C5

The salt solutions used as solvents for the crown ether dissolution (the concentration  $c_{NaI} = (0.049 \pm 0.001) \text{ mol dm}^{-3}$ ) were obtained by dissolving an appropriate amount of NaI in a freshly prepared solvent. The solution enthalpy of 15C5 in the DMA–water–NaI system was measured at 298.15 K using “isoperibol” type calorimeter at  $(298.15 \pm 0.005) \text{ K}$  as described in an earlier report [13]. The calorimeter was calibrated on the basis of the standard enthalpy of solution at the infinite dilution of urea (Calorimetric standard U.S., NBS) in water at 298.15 K. The value obtained from ten

measurements in this study was  $(15.30 \pm 0.07) \text{ kJ mol}^{-1}$  (literature data  $15.31 \text{ kJ mol}^{-1}$  [14],  $15.28 \text{ kJ mol}^{-1}$  [15]). Thus uncertainties in the measured enthalpies did not exceed  $\pm 0.7\%$  of the measured value. Six–eight independent measurements were performed on each investigated system. The final concentration of the 15C5 solutions ranged from  $0.00318 \text{ mol dm}^{-3}$  to  $0.00870 \text{ mol dm}^{-3}$ . No concentration dependence (outside the error limits) of the enthalpies of dissolution was observed because of a too small range of the concentration of 15C5 and consequently the mean values are given in Table 2. The dissolution enthalpies of 15C5 in the DMA–water–NaI system,  $\Delta_{sol}H_2$ , presented in this paper and those in the mixtures of water with DMA taken from a earlier publication [6] are shown in Figure 1 as functions of water contents in the mixture,  $x_w$ .

As is seen in Figure 1, the difference in the course of the both functions in the DMA–water mixture confirms the formation of 15C5/Na<sup>+</sup> complex [1–4].

## Results and discussion

### The thermodynamic function of the complex formation

The equilibrium constant of the complex formation,  $K_f$ , and thermodynamic standard functions of the 15C5/Na<sup>+</sup> complex formation: free energy,  $\Delta_f G^0$ , enthalpy,  $\Delta_f H^0$ , and entropy,  $T\Delta_f S^0$  were calculated as in previous papers [1–4]. They are presented in Table 2 and in Figure 2 as functions of  $x_w$ . For comparison purposes Figure 2 also shows analogous functions of 15C5/Na<sup>+</sup> formation in the DMF–water mixture [4].

As is seen, the standard functions of 15C5/Na<sup>+</sup> complex formation in DMA–water mixture are negative. Hence it follows that the process of complex formation is the enthalpy-stabilized. The courses of the thermodynamic functions of 15C5/Na<sup>+</sup> complex formation in DMA–water and DMF–water mixtures [4] are similar. The values of  $\Delta_f G^0$  in the DMA–water mixture are less negative than those in the DMF–water but the values of  $\Delta_f H^0$  and  $T\Delta_f S^0$  are more negative in the DMA–water mixture. The functions  $\Delta_f H^0 = f(x_w)$  and  $T\Delta_f S^0 = f(x_w)$  reach the most negative values at  $x_w = 0.7$  in the mixed solvent DMA–water. In DMF–water, the minimum of these functions is at  $x_w = 0.6$  and is more shallow than that for the DMA–water mixture. The observed differences in the position and depth of the minimum are probably associated with different properties of the mixtures under discussion. Different values of partial molar heat capacity,  $C_{p_2}^0$ , the slope of apparent molar volume *versus* the molarity of organic substance,  $V_{\phi_{22}}$ , the enthalpic homogeneous pair interaction coefficient,  $h_{22}$ , for the substance in water (they are a hydrophobicity measure of the substance in water [16–18]) indicate that DMA is more hydrophobic than DMF [19]. Thus, one may assume that the

Table 1. Molar conductances of 15C5–NaI system in the DMA–water mixtures at 298.15 K

$x_w = 0.0$		$x_w = 0.2$		$x_w = 0.4$		$x_w = 0.5$	
mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$
0.0000	64.415	0.0000	47.302	0.0000	32.642	0.0000	27.391
0.1364	64.411	0.2299	47.296	0.2055	32.625	0.2262	27.366
0.3231	64.406	0.4483	47.290	0.4658	32.605	0.4167	27.346
0.4615	64.402	0.6552	47.285	0.6986	32.587	0.6548	27.319
0.6000	64.398	0.7931	47.281	1.0137	32.564	0.8333	27.302
0.7538	64.394	0.9195	47.278	1.2192	32.548	1.0361	27.283
0.9692	64.388	1.1149	47.274	1.5068	32.527	1.1205	27.265
1.1846	64.382	1.2874	47.269	1.7123	32.514	1.3494	27.251
1.3231	64.379	1.4253	47.266	1.9178	32.501	1.5301	27.232
1.4923	64.374	1.6207	47.262	2.0685	32.490	1.7831	27.210
1.6154	64.371	1.7701	47.259	2.3014	32.473	1.9277	27.195
1.7846	64.367	1.9310	47.255	2.4795	32.463	2.1446	27.175
1.9231	64.363	2.0805	47.252	2.6438	32.452	2.3373	27.158
2.1077	64.359	2.2989	47.247	2.8356	32.438	2.4940	27.143
2.2462	64.356	2.5172	47.243	3.0959	32.421	2.6145	27.132
2.4154	64.351	2.6897	47.239	3.2877	32.410	2.8193	27.114
2.5538	64.349	2.8851	47.235	3.4521	32.401	3.0000	27.099
2.7231	64.344	3.0460	47.232	3.6027	32.391	3.1928	27.083
2.8615	64.341	3.1839	47.229	3.7534	32.380	3.3373	27.071
3.0308	64.337	3.4023	47.225	3.8904	32.372	3.5060	27.058
3.1692	64.334	3.5747	47.221	4.0959	32.360	3.6988	27.040
3.3692	64.330	3.7931	47.217	4.2740	32.351	3.9398	27.021
3.6154	64.324	4.0345	47.213	4.4658	32.340	4.0843	27.009
3.8000	64.320	4.3488	47.208	4.6164	32.331	4.2410	26.996
4.0154	64.315	4.6163	47.203	4.7260	32.324	4.4458	26.980
4.2462	64.311	4.8488	47.199	4.8356	32.318	4.5904	26.969
4.5231	64.305	5.1279	47.194	5.0972	32.307	4.7349	26.957
4.7538	64.300	5.4419	47.189	5.3472	32.293	4.8675	26.948
5.0308	64.295	5.6163	47.186	5.6944	32.275	5.0843	26.933
5.2923	64.289	5.7907	47.184	6.2083	32.250	5.5181	26.901
5.6769	64.282	6.1395	47.178			5.9518	26.872
$x_w = 0.6$		$x_w = 0.7$		$x_w = 0.8$		$x_w = 0.9$	
mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$
0.0000	24.290	0.0000	23.409	0.0000	28.338	0.0000	45.579
0.1125	24.264	0.1795	23.361	0.1882	28.301	0.2105	45.557
0.3125	24.221	0.4359	23.287	0.4118	28.249	0.4342	45.535
0.5250	24.176	0.6154	23.241	0.5765	28.221	0.6447	45.512
0.7500	24.126	0.7949	23.191	0.7765	28.177	0.8158	45.495
0.9500	24.084	0.9487	23.153	0.9294	28.151	1.0658	45.469
1.1750	24.040	1.1667	23.096	1.1412	28.109	1.2368	45.452
1.4250	23.988	1.3846	23.041	1.3294	28.071	1.4211	45.433
1.5875	23.955	1.5128	23.008	1.4941	28.030	1.6133	45.417
1.8125	23.913	1.7564	22.946	1.7412	27.988	1.8267	45.395
2.1000	23.855	2.0000	22.887	1.9412	27.948	2.0267	45.374
2.3625	23.807	2.1538	22.851	2.1529	27.912	2.2267	45.353
2.6750	23.749	2.3718	22.788	2.4000	27.863	2.3867	45.338
2.8625	23.713	2.5000	22.764	2.6000	27.821	2.6133	45.314
3.0500	23.678	2.7143	22.724	2.7647	27.793	2.8133	45.295
3.2375	23.645	2.8442	22.691	2.9882	27.748	2.9867	45.282
3.3375	23.626	3.0130	22.655	3.1412	27.718	3.1733	45.262
3.5125	23.595	3.1688	22.616	3.2824	27.691	3.3867	45.239
3.6875	23.568	3.3247	22.582	3.4353	27.670	3.6000	45.219
3.8500	23.536	3.4545	22.549	3.5882	27.644	3.8400	45.196
3.9875	23.514	3.6364	22.513	3.7176	27.613	4.0133	45.180
4.1250	23.492	3.7792	22.476	3.9405	27.582	4.2000	45.158
4.2875	23.464	3.9740	22.436	4.0714	27.556	4.4800	45.134

Table 1. (continued)

$x_w = 0.6$		$x_w = 0.7$		$x_w = 0.8$		$x_w = 0.9$	
mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$	mr	$\Lambda_{\text{obs}}$
4.4000	23.446	4.1558	22.394	4.2024	27.543	4.7333	45.106
4.5125	23.432	4.3636	22.353	4.3333	27.511	5.0400	45.081
4.6125	23.414	4.6753	22.289	4.4881	27.490	5.3600	45.048
4.7750	23.391	4.9481	22.231	4.6310	27.463	5.5867	45.028
4.9250	23.366	5.3896	22.140	4.8690	27.420	6.0000	44.991
5.2785	23.322	5.8182	22.059	5.0952	27.380	6.3067	44.963
5.6709	23.263			5.4881	27.310		45.579
6.1266	23.206			6.0952	27.218		45.557

$x_w$  – molar fraction of water in the mixtures; mr = molar ratio  $c_{15C5}/c_{NaI}$ ; unit  $\Lambda$ :  $S \text{ cm}^2 \text{ mol}^{-1}$ .

Table 2. The equilibrium constants,  $K_f$ , the thermodynamic functions of complex formation:  $\Delta_f G^0$  ( $\text{kJ mol}^{-1}$ ),  $\Delta_f H^0$  ( $\text{kJ mol}^{-1}$ ),  $T\Delta_f S^0$  ( $\text{kJ mol}^{-1}$ ) in DMA–water mixtures and the enthalpy of solution of 15C5 in DMA–water–NaI system,  $\Delta_{\text{sol}}H_2$  ( $\text{kJ mol}^{-1}$ ), at 298.15 K

$x_w$	$K_f$	$\Delta_f G^0$	$\Delta_f H^0$	$T\Delta_f S^0$	$\Delta_{\text{sol}}H_2$
0.0	$68.73 \pm 1.47$	-10.49	-15.67	-5.19	$-10.96 \pm 0.05$
0.1	66.12 <sup>a</sup>	-10.39	-18.08	-7.69	$-11.64 \pm 0.02$
0.2	$63.64 \pm 1.26$	-10.30	-21.29	-11.00	$-13.00 \pm 0.07$
0.3	61.49 <sup>a</sup>	-10.21	-25.23	-15.02	$-14.61 \pm 0.08$
0.4	$59.26 \pm 1.18$	-10.12	-28.68	-18.56	$-15.80 \pm 0.06$
0.5	$56.45 \pm 0.77$	-10.00	-32.92	-22.92	$-17.97 \pm 0.05$
0.6	$56.13 \pm 1.25$	-9.98	-35.56	-25.58	$-20.74 \pm 0.04$
0.7	$43.35 \pm 0.88$	-9.34	-35.76	-26.41	$-23.64 \pm 0.05$
0.8	$23.16 \pm 1.20$	-7.79	-31.49	-23.70	$-25.36 \pm 0.06$
0.9	$10.51 \pm 0.87$	-5.83	-21.19	-15.36	$-30.30 \pm 0.05$
1.0		-3.11 <sup>b</sup>	-4.86 <sup>b</sup>	-1.75 <sup>b</sup>	$-41.35 \pm 0.06$

<sup>a</sup>Interpolated value from equation:  $\Delta_f G^0 = -10.49271(0.01048) + 0.96441(0.03125)x_w$  for  $0 \leq x_w \leq 0.5$ ,  $r^2 = 0.9979$ .

<sup>b</sup>From Ref. [1].

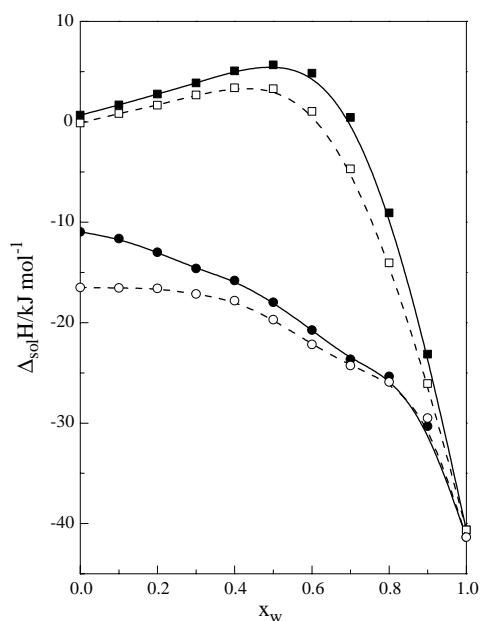


Figure 1. The dissolution enthalpy of 15C5 in: DMA–water–NaI (■) (this paper), DMA–water mixtures (●) (from Ref. [6]), DMF–water–NaI (○) (from Ref. [4]), DMF–water mixtures (□) (from Ref. [6]), at 298.15 K.

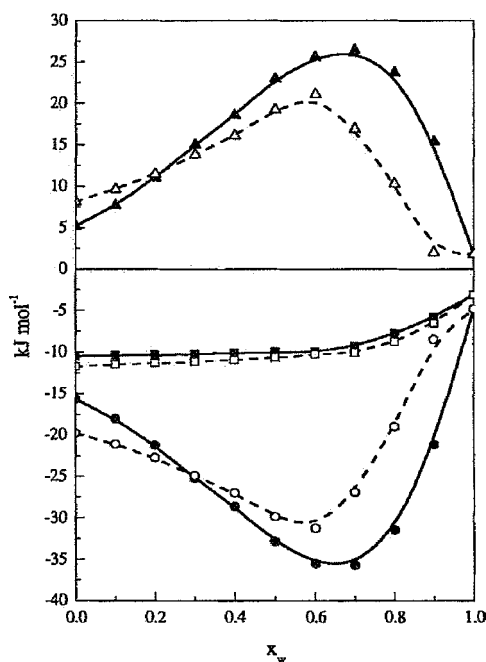


Figure 2. Thermodynamic functions of 15C5/ $\text{Na}^+$  complex formation:  $\Delta_f G^0$  (■),  $\Delta_f H^0$  (●) and  $-T\Delta_f S^0$  (▲) in DMA–water mixtures;  $\Delta_f G^0$  (□),  $\Delta_f H^0$  (○) and  $-T\Delta_f S^0$  (Δ) in DMF–water mixtures (from Ref. [4]) at 298.15 K.

difference in the depth and position of the minimum of the functions  $\Delta_f H^0 = f(x_w)$  and  $T\Delta_f S^0 = f(x_w)$  is closely connected with different hydrophobic properties of DMA and DMF and consequently with the different structures of the mixtures and energetic properties of the interactions between water and DMA or DMF. A parameter that describes the structural properties or so-called structuredness of the mixture is the excess molar volume of the mixture,  $V^E = f(x_w)$ , while the parameter that describes the energetic of the interactions in the mixture is the excess molar heat of mixing water with organic solvent,  $H^E = f(x_w)$ . The data concerning the functions  $V^E = f(x_w)$  and  $H^E = f(x_w)$  applying to the mixture of water with DMA, DMF and DMSO, were calculated from data in the literature [20, 21, 10, 22, 23] and the values of functions at the given composition of the mixture were calculated with the use of the commonly known Redlich–Kister equation. It has been observed that the excess enthalpy and entropy of com-

plex formation as the functions of  $x_w$ ,  $\Delta_f H^E = f(x_w)$  and  $T\Delta_f S^E = f(x_w)$ , correlate with the function  $V^E = f(x_w)$  and  $H^E = f(x_w)$  within the whole composition range of the mixed solvents: DMA–water, DMF–water and DMSO–water according to Equations (1) and (2):

$$\Delta_f H^E = aV^E + bH^E \quad (1)$$

$$T\Delta_f S^E = dV^E + eH^E \quad (2)$$

The graphical illustrations of Equations (1) and (2) are shown in Figure 3.

In the case of all the mixed solvents shown in Figure 3, it is seen that the influence of the structural properties of the mixture and the energetic effects of the interactions in the mixtures play a significant part in the process of 15C5/Na<sup>+</sup> formation as they directly influence the solvation of the complex-forming components, i.e., 15C5 and Na<sup>+</sup>. In the mixtures of water with DMF

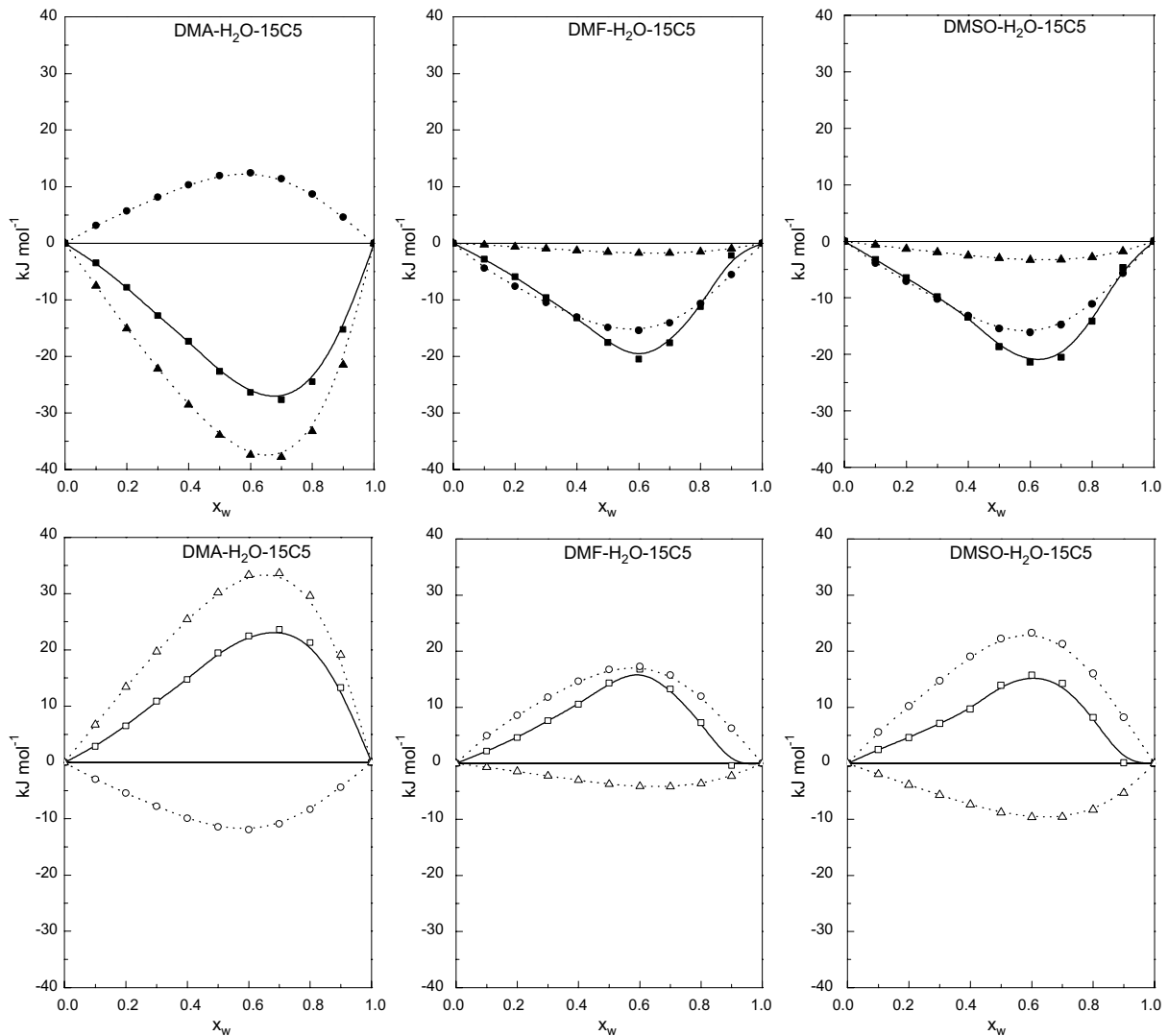


Figure 3. Graphical illustration of Equation (1):  $\Delta_f H^E$  (■),  $aV^E$  (●),  $bH^E$  (▲) and Equation (2):  $-T\Delta_f S^E$  (□),  $-cV^E$  (○),  $-bH^E$  (Δ) for 15C5/Na<sup>+</sup> in the mixtures of water with DMA, DMF, and DMSO.

and DMSO which are regarded as neutral (with no hydrophobic or hydrophilic properties) [24, 25], energetic effects influence the enthalpy and entropy of complex formation only to a small extent. On the other hand, the structuredness of the mixture ( $V^E = f(x_w)$ ) affects beneficially the enthalpy and disadvantageously the entropy of complex formation. In the case of a hydrophobic mixed solvent such as DMA–water, a reverse situation is observed, i.e., the structuredness of the mixture ( $V^E = f(x_w)$ ) affects disadvantageously the enthalpy and beneficially the entropy of complex formation, but the energetic effects exceed the structural effects. The observed differences in the influence of particular effects on the enthalpy and entropy of complex formation are most probably connected with the phenomenon of hydrophobic hydration of DMA.

Using the functions  $\Delta_f H^0 = f(x_w)$  and  $T\Delta_f S^0 = f(x_w)$  for  $15C5/Na^+$  in the DMA–water mixture it is possible to calculate the parameters of the linear dependence presented by Equation (3) known from the literature [26–29] as in the case of  $15C5/Na^+$  and  $B15C5/Na^+$  in the mixtures of water with DMSO and DMF [1, 2, 4]:

$$T\Delta_f S^0 = T\Delta_f S_0 + \alpha\Delta_f H^0. \quad (3)$$

The value of  $T\Delta_f S_0$  connected with desolvation of  $Na^+$  is, within the error limits, the same for the  $15C5/Na^+$  formation in water–DMSO, water–DMF and water–DMA and amounts to  $(4.77 \pm 0.77)$  kJ mol<sup>-1</sup>. This observation seems to be reflected in the enthalpy of  $Na^+$  solvation that is similar in these mixtures [1, 4; for DMA–water mixture see below]. Parameter  $\alpha$  is also the same within the error limits and amounts to  $0.783 \pm 0.073$ , which means that in all systems under consideration the same percentage of the beneficial enthalpic contribution to the complex formation is used to recompense for the disadvantageous entropic share. Based on the above observations, one may assume that parameter  $\alpha$  does not depend on the type of solvent used in these considerations.

#### Enthalpies of solvation of $15C5/Na^+$ complexes in DMA–water mixtures

The enthalpy of complex solvation was analysed on the basis of transfer enthalpy of the complex from water (W) to the mixture DMA–water (M) similar as in previous papers [1–4, 9] (Equation 4).

$$\Delta_{tr}H_{15C5/Na^+}(W \rightarrow M) = \delta\Delta_f H_{(s)} + \Delta_{tr}H_{15C5}(W \rightarrow M) + \Delta_{tr}H_{Na^+}(W \rightarrow M), \quad (4)$$

where  $\Delta_{tr}H_{15C5/Na^+}(W \rightarrow M)$ ,  $\Delta_{tr}H_{15C5}(W \rightarrow M)$ ,  $\Delta_{tr}H_{Na^+}(W \rightarrow M)$  are the transfer enthalpies of  $15C5/Na^+$ ,  $15C5$  and  $Na^+$ , respectively, from water to the mixed water–organic solvent;  $\delta\Delta_f H_{(s)}$  is the difference

between the enthalpy of complex formation in the water–organic mixed solvent and that in water.

The transfer enthalpy of  $Na^+$  was found on the basis of the relation  $\Delta_{tr}H_{(Cs^+)} = \Delta_{tr}H_{(I^-)}$  using data for the enthalpy of the solution of electrolytes in DMA–water mixtures given in a paper by Taniewska-Osińska and Tkaczyk [30]. Figure 4 illustrates all components of Equation (4) as a function of  $x_w$  in the water–DMA and water–DMF mixtures.

As is seen, the exothermicity of the enthalpy of complex solvation increases with increasing the water content in the mixture. Analysing the curves shown in Figure 4, one can see that the enthalpy of the  $15C5/Na^+$  complex formation in the water–DMA mixture with low and medium water contents ( $x_w < 0.6$ ) is affected mainly by the function  $\delta\Delta_f H_{(s)} = f(x_w)$ . In the mixture with  $x_w > 0.6$ , first of all the ligand solvation is the dominating process in the complex solvation. Thus, this situation is different from that observed in the mixture of water with DMSO or DMF, where the  $15C5$  solvation is a main factor that influences the complex solvation within the whole range of mixed solvent [1, 4]. On the other hand, in the mixture of water with AN, the solvation enthalpy of the  $15C5/Na^+$  complex versus the mixed solvent composition depends mostly on the enthalpy of  $Na^+$  solvation [3]. The observed differences are connected first of all with different properties of mixed water–organic solvents as well as pure organic solvents. One should bear in mind that DMSO, DMF, DMA and AN are aprotic solvents, with the first three

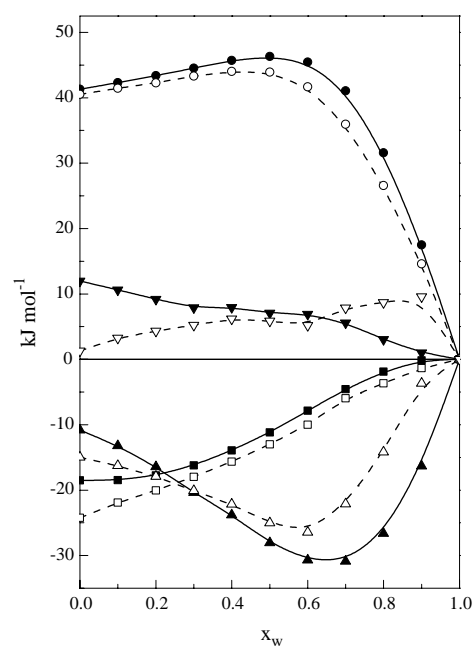


Figure 4. The transfer enthalpy of chemical individuals from water to water–DMA mixtures:  $\Delta_{tr}H_{Na^+}^0$  (■),  $\Delta_{tr}H_{15C5}^0$  (●) and  $\Delta_{tr}H_{15C5/Na^+}^0$  (▼) and the factor  $\delta\Delta_f H_{(s)}^0$  (▲); from water to water–DMF mixtures:  $\Delta_{tr}H_{Na^+}^0$  (□),  $\Delta_{tr}H_{15C5}^0$  (○) and  $\Delta_{tr}H_{15C5/Na^+}^0$  (▽) and the factor  $\delta\Delta_f H_{(s)}^0$  (△) (from Ref. [4]).

of them showing dominating base properties and the latter possessing acidic properties.

### Conclusions

In the mixture of water with DMA, the 15C5/Na<sup>+</sup> complexes are enthalpy stabilized. The excess enthalpy and entropy of 15C5/Na<sup>+</sup> complex formation depend quantitatively on the structural and energetic properties of interactions in the water–DMA mixture within the whole composition range of the mixed solvent.

A very good entropy–enthalpy correlation of the 15C5/Na<sup>+</sup> complex formation is observed in the mixture of water with DMA. The value of  $T\Delta_f S_0$  connected with desolvation of Na<sup>+</sup> during of complex formation is the same in water–DMSO, water–DMF and water–DMA and amounts to  $(4.77 \pm 0.77)$  kJ mol<sup>-1</sup>. The same percentage of the beneficial enthalpic contribution to the complex formation is used to recompense for the disadvantageous entropic share in the mixtures of water with DMA, DMF and DMSO.

The enthalpy of 15C5/Na<sup>+</sup> complex solvation depends on the enthalpy of complex formation in the mixture with a low or medium water content as well as on the enthalpy of ligand solvation in the water–DMA mixture within the water-rich region.

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